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# Remote Sensing of Hydrocarbons and Toxic Pollutants Workshop Minutes. Held in Las Vegas, Nevada on April 6-7, 1989

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# REMOTE SENSING OF HYDROCARBONS AND TOXIC POLLUTANTS: (WORKSHOP MINUTES)

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Cooperative Agreement No. CR814002

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16. ABSTRACT A number of remote sensing techniques are now available for monitoring hydrocarbons and toxic airborne pollutants. Filter and dispersive spectroradiometers (line integral in ppb range; cost about $35K) with restricted versatility are sold commercially. The more versatile FTIR's (line integral in ppb range; cost $50-100K) and DIAL's (range-resolve in ppm range; cost $100-200K) are now becoming commercially available. Automatic, unattended field operation has been successfully demonstrated for several types of such adaptable remote sensing systems. FTIR's and DIAL's complement each other in identifying a pollutant's presence and its spatial extent; there is potential for improving their performance by a factor of ten or more in the next ten years. Much of the promise for FTIR's lies in their reliance on computer software and hardware to perform the frequency analyses and to access the stored libraries of reference spectra. In both of these areas we can expect significant advances and cost cuts in the next ten years, judging from the past ten. Gains in optical hardware and radiation sources will also enhance FTIR performance. No "breakthrough" component development is required to enhance their present quite adequate capabilities. DIAL performance can also be enhanced over the next ten years by about one order of magnitude with no breakthroughs. If avalanche photodiodes for the thermal infrared can be made feasible for field work, there is a potential for an additional order of magnitude or more of performance improvement. Rapid line-tuning will be easier as the development of optical modulators for the infrared progresses.

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## FOREWORD

In April 1989, a workshop was held in Las Vegas, Nevada, to consider how emerging remote sensing technology could be used for the detection and mapping of toxic air pollutants and hydrocarbons in the atmosphere and applied to the solution of priority environmental problems. The meeting was sponsored jointly by the University of Nevada-Las Vegas's Environmental Research Center and the Environmental Monitoring Systems Laboratory-Las Vegas. The attendees were scientists and engineers from these groups, other Federal agencies, universities (domestic and foreign), and private companies (domestic and foreign) actively involved in research and development of the relevant remote sensing technologies. Representatives from several Regions also attended the workshop to act as observers and to provide the perspective of potential clients for the technology.

This report is the result of that workshop. It summarizes the relevant technologies and the capabilities of candidate remote sensors; a representative list of such sensors, their capabilities and characteristics, and their geographical locations are presented for reference. The report also compares the technologies for future performance capabilities, ease of operation, and cost over the next five to ten years. As such, information contained in the report should aid the Agency in formulating plans for sensor research and development for dealing with important regulatory and research issues facing it.

The report was assembled from inputs developed at the workshop and after it by all of the participants. A draft of the report was circulated for final comment by the participants. The result is, therefore, a group effort by the attendees, who are listed in the appendices. The views expressed are the informed views of the attendees and not necessarily those of the organizations they represent.

James L. McElroy
Project Officer

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## Preface

This is a report on the significant advantages of remote sensors for detecting and mapping airborne hydrocarbons and toxic pollutants. The report is essentially the minutes of a workshop on this topic held in Las Vegas, Nevada, on April 6-7, 1989. All of the participants at the workshop have contributed to this report. A glossary of acronyms and remote sensing terms is given in Appendix 1. Sensor performance described in detail in Appendices 2-5 is achieved with remote sensors that already exist in 1989. The sophistication of the remote sensing discipline is not widely appreciated because of its rapid maturity in the past ten years. This growth has been possible thanks to:

- Spectacular advances in digital computers and data processors, and
- Improvements in optical components and laser technology, largely the result of DOD and NASA programs.

Remote sensing as a monitoring tool is available and ready to assist the U.S. EPA in documenting and solving many of its most pressing air-related problems. This is a problem-focused report. For example, the many cities with Clean Air Act nonattainment for ozone levels likely have emissions of precursor hydrocarbons that differ considerably from (and are generally higher than) those predicted using engineering models for inclusion in emission inventories. The California tunnel experiment (Ingalls, 1989; Stockberger et al., 1989) demonstrated that tailpipe hydrocarbons were two to seven times higher than expected. Grab samples in the open environment can never provide the complete picture of the merging plumes from natural and anthropogenic sources into the ambient background. A properly designed suite of remote

sensors can paint the big picture, providing real-time, spatially resolved air quality data!

## 1. Executive Summary

Remote sensing technology is now ready and able to play a significant role in EPA programs such as TSCA, EMAP, RCRA, and Clean Air Act compliance. By their very nature, remote sensors unravel many of the difficult pollution monitoring problems by:

- Measuring representative, volume-averaged samples;
- Documenting the extent of hydrocarbons or toxic gaseous pollutants;
- Providing reduced data to the investigator in the field in real time; and,
- Eliminating the need to capture samples that need to be returned to the laboratory for analysis.

Remote sensors utilize the absorption, emission, or fluorescence spectra of pollutants (and each pollutant has its own, unique, identifying spectrum) to identify unambiguously the chemical constituents in the atmosphere. Thus the possibility of overlooking an unexpected contaminant is minimized. Many of the present-day remote sensors can sort out and identify a specified pollutant from the "urban soup" consisting of multitudes of compounds. Such off-the-shelf sensors as listed in Appendix 2 have demonstrated detection sensitivities that already meet EPA needs and monitoring requirements.

There are two types of remote sensors that can already meet EPA necessities: Spectroradiometers, and Laser Radars or Lidars. Many examples of both types of sensors are in everyday use, and some have passed the stringent type-testing requirements of the U.S. Army and Navy. They are <u>not</u> "ivory tower" instruments or future goals of dreamy-eyed researchers.

There are several functions that remote sensors can provide without the necessity of physically entering private, restricted or hazardous areas:

- Monitoring emissions from point sources such as stacks;
- Defining the amount of pollutant that crosses a defined fenceline, for example, one that surrounds a refinery;
- Measuring ambient concentrations of pollutants over path lengths as short as a few meters to as long as many kilometers.

Present-day lidar remote sensors (described more completely in Appendix 4) are able to detect, identify, and range-resolve toxic pollutants in the parts-per-million (ppm) range. Spectroradiometers (Appendix 3) can detect, identify and quantify line integral averages of toxic pollutants in the parts-per-billion (ppb) range. Of the spectroradiometers, the Fourier-transform, infrared devices (FTIR's) have the unique ability to identify quickly those pollutants present by performing real-time transforms and matching the detected spectra against stored libraries of pollutant spectra. Multidetector ultraviolet (UV), dispersive instruments used with xenon-arc sources also show much promise although they have not been widely used to date. Laser sources that may be tuned to desired absorption or "window" lines may also be used, eliminating the need for spectral discrimination or dispersion in the radiometer. All of these sensors are available today - no basic research is required in order to apply their proven capabilities. Costs of the spectroradiometers range from $35K for the more simple, hand-held devices to perhaps $100K for versatile, mobile units. Lidars run in the $100K to $200K price range, being somewhat more complex instruments.

It is now possible to deploy in the field, as hand-held, mobile or airborne instruments, either singly or in suites, such lidars and spectroradiometers that will complement each other's performance. FTIR output data can be used to instruct a tunable laser source, in a differential absorption lidar (DIAL), what wavelengths to use to range resolve the pollutant for better definition of its spatial extent. These two instruments, especially when used together, seem to hold the most promise for field-deployed hydrocarbon and toxic pollutant remote sensors, now, into the 1990's, and beyond.

Even though present-day remote sensors have demonstrated versatile and reliable performance, improvements are possible. Over the next ten years, the detection sensitivity of spectroradiometers will be improved by a factor of ten (10 dB) as detailed in Appendix 6. Increases in computer speed, memory, and software sophistication will also significantly improve FTIR performance. Similar enhancements in lidar performance by 10 dB in sensitivity and in rapid tuning and pollutant identification accomplishments will be possible, even with no "breakthrough" developments in components. Remote sensors will be able to provide the monitoring sensitivities necessary even as clean air requirements become more stringent in the future. Future remote sensor costs should not radically increase (in 1989 dollars).

## 2. Objectives of the Report

Air pollution by ozone-precursor hydrocarbons or other toxic compounds is a problem on the local, regional, and global scale. Many EPA concerns, such as TSCA, EMAP, RCRA, Alternate Fuels, and the more general matters of acid rain and acid aerosols, stratospheric ozone depletion, global climate change, and the sick building syndrome are affected by hydrocarbons and toxics. The Clean Air Act requires that pollutant nonattainment areas be characterized quantitatively and strategies be developed for attainment of the relevant air quality standards. There is clearly a need for effective, real-time monitoring on all geographic scales. The objectives of this report are to demonstrate why and how remote sensing technology is now ready to help fulfill this need.

In addition to the day-to-day ambient pollution in urban areas, hydrocarbon and toxic spills or the escape of such vapors and gases have become so common as to be hardly newsworthy. Almost every train derailment seems to produce such an event. Industrial accidents and fires force the evacuation of neighborhoods, even whole cities because toxic fumes or smoke threaten safety over wide areas. Are all such evacuations necessary? Are the areas where exposure will be dangerous alerted sufficiently in advance or at all? When health problems arise in the aftermath of such occurrences, is it possible to determine if the toxic exposure was to blame? What chemical transformations occur as such pollutants are transported in plumes or air masses across local and regional boundaries?

Ideally, public officials would be able to predict for the day-to-day ambient conditions or during the course of an accident when, where, and at what level the harmful constituents will exist, and be able later to say exactly where and at what level some potentially dangerous pollutant did exist. There is the additional problem of measuring the even lower concentration but more persistent hydrocarbon or toxic emissions from landfills. Such a service to the public cannot now be provided. In this report we concentrate on existing remote sensing technology that shows promise for supporting such a service in the future. We focus on remote sensing because we need measurement techniques that can cover large volumes in space in a short time, techniques that can determine where a plume was and where it was not and that do not require entry into areas already impacted by the problem.

As an example, the Superfund mandate requires assessment, characterization, and cleanup of hazardous waste sites. An active or passive FTIR can be used for rapid characterization by measuring absorption spectra along multiple paths that crisscross the site. Just five minutes of measurement and analysis time for each path provides the data to produce rapidly a map of the site with isopleths showing contaminated regions. This procedure would pinpoint areas where more expensive contract laboratory procedures (CLP) might be needed, eliminating the large costs and time required for CLP where there was no contamination.

Hazardous waste incinerator emissions can be monitored by FTIR's in under two minutes compared to weeks required for gas chromatograph (GC) or

mass spectrometer (MS) procedures. Quantitative agreements of FTIR's with GC and MS were recently demonstrated (McLaren et al., 1989).

A laser SAR (source-augmented radiometer) using retroreflectors to redirect the laser beam back to the instrument can be set up conveniently along the fenceline of an area to be monitored. Pollutants that advect with the wind out of the site cross the laser beam. The laser wavelengths are selected so that one is absorbed and one is not, provided a differential detection signature. This method has been proven during numerous experiments, and is nov used routinely by major chemical plants as a safety monitor.

We hope to demonstrate in the remainder of the report that such remote sensing technology, discussed briefly above, offers a viable method for the U.S. EPA to utilize in enhancing the performance of its mission.

## 3. Remote Sensing Advantages and Characteristics

We define remote sensing as the measurement of a target constituent by means of wave energy interaction with the target, using an instrument at some distance from the target. For hydrocarbons or toxic pollutants the waves will most likely be electromagnetic, for acoustic waves do not have a strong discrimination ability for most gases or vapors. The electro-magnetic remote sensor exploits differences in absorption, emission, fluorescence, or scattering between the target constituent and the surrounding atmosphere to identify the pollutant and to quantify its concentration.

The advantages that remote sensors have over in situ sensors are the following:

- More representative sampling because of volume averaging.
- One sensor can sample a large volume, over many different lines-of-sight, and at the speed of light.
- One sensor can be used to sample for multiple pollutants by adjusting its operating frequency or through selective data analysis whereas most current EPA methods are pollutant specific with each requiring a different method.
- Measurement results can be available in real time, in the field if desired.
- Mapping for hot-spots of pollutants is possible quickly.
- Stand-off measurements are possible - no need to enter hazardous or restricted sites.
- Can be on-line 24 hours per day.
- There is a proven base of technology, paid for largely by the DOD and by NASA.

- Costs for the complete series of measurements to characterize a site can be kept low through the expedient of scanning, volume sampling, and real-time data analysis.
- Can show the absence of known materials in the beam.
- Can be used as real-time monitors to tell when in situ sensors have a chance of measuring other than zero concentrations.
- Reactive or unstable gas constituents can be measured without sampling problems inherent in capture techniques.
- Problems with surface adsorption and time delays avoided.
- Rapid field calibrations allow quantitative measurements.

Details on how many of these various advantages are accomplished are given in Appendices 2 - 5 in this report.

Before presenting more information on the characteristics of appropriate remote sensors, it is helpful to define sensor performance. There are many ways to describe the detection sensitivity of sensors - in parts-per-million or -per-billion by volume or by mass, in mass of pollutant per mass or volume of air, or by path integrated concentrations, particularly for those sensors which intrinsically average over their light path. For path-integrated concentrations, one part-per-million in a 1-m path produces the same absorption as one part-per-billion in a 1-km path, or 1 ppm-m = 1 ppb-km. Note that 1 ppm for an ideal gas is 1 ppmv(by volume or by molecules). This mixing ratio is independent of pressure, temperature, and molecular weight.

At a temperature of 273°K and a pressure of one atmosphere, a gram-molecule of gas or mol occupies 22.4 l and contains $6.02 \times 10^{23}$ molecules (Avogadro's number), so the number of molecules, $n_o$, in 1 ml is

$$n_o = 6.02 \times 10^{23} / 22{,}400 = 2.69 \times 10^{19}.$$

At 298°K this number is $2.5 \times 10^{19}$ molecules per ml, so 1 ppm = $2.5 \times 10^{13}$ molecules/ml path integrated, so (since 1 ml = 1 $cm^3$)

$$1 \text{ ppm-m} = 2.5 \times 10^{13} \times 100 \text{ cm} = 2.5 \times 10^{15} \text{ molecules/cm}^2.$$

Taking for example benzene, molecular weight (M.W.) of 78,

$$1 \text{ ppm-m} = 1 \text{ ppb-km} = \frac{2.5 \times 10^{15} \times 78}{6.0 \times 10^{23}} = 3.3 \times 10^{-7} \text{ gm cm}^{-2}$$

or for any temperature T(K) and pressure P(Atm), the conversion is

$$1 \text{ ppm-m} = \frac{\text{M.W.} \times 10^{-4}}{22{,}400} \times \frac{273}{T(K)} \times P(\text{Atm}) \text{ gm cm}^{-2}.$$

It is hoped that these conversion relationships, provided by Donald Stedman, will be found useful when comparing sensing instruments whose performance may be described using different measures of sensitivity.

Remote sensors for airborne hydrocarbons or toxics fall naturally into two classes - spectroradiometers or lidars. A short description is provided here of each class of sensor with advantages of each. More detailed information is given in Appendices 2-7.

A spectroradiometer is a radiation-measuring device (a radiometer) that is able to identify a pollutant by discriminating the spectrum of the radiation that it absorbs, scatters, or emits. The radiation that is absorbed may come from the naturally occurring background of sunlight or thermal emission, in which case the instrument is a "passive sensor," or it may come from a supplied source of radiation such as a lamp or glower. The spectral discrimination may be provided by an absorption or interference filter, it may be supplied by a dispersing element (a prism or a diffraction grating), or a scanning interferometer may be used.

Spectroradiometers may be packaged into small, rugged units - even hand-held devices are possible. The technology is well developed and proven in the field. Costs can be in the $35K to $100K range. Operation can be quite simple. They can monitor fencelines, or can be used to scan an area, providing an integrated measure of the target pollutant(s) along the line-of-sight. Appendix 3 provides more details on spectroradiometers.

Lidars use laser sources to irradiate an air volume; the backscattered or retroreflected radiation is then analyzed to detect and identify pollutant. A DIfferential Absorption Lidar (DIAL) utilizes at least two wavelengths from the laser, at least one of which is absorbed by the pollutant, and one of which falls in a "window" in the pollutant absorption spectrum. Frequency modulated (FM) lidars modulate the laser so that the modulation frequency appears as two sidebands on the laser line frequency. If the laser is operated near the edge of a pollutant absorption line, the sidebands will be differentially affected. Raman lidars utilize the Raman shift in frequency of

the backscattered radiation that is a characteristic of the pollutant being measured.

Lidars tend to be more complex instruments than spectroradiometers. However, they can provide range-resolved data on the concentration of pollutants without requiring retroreflectors. They can therefore be used to document plume dispersion models when the lidar is advantageously placed to be able to scan large volumes of the plume. Airborne lidars are ideal instruments for investigating long-range transport of aerosols in plumes. Range resolution as fine as several meters is available with many instruments. Mobile lidars in small vans have been used for years in air pollution studies, so there is a substantial foundation of experience to draw upon. Lidar costs are in the $100K and up range, depending on the versatility designed into the instrument, but one lidar may be able to replace many in situ instruments. The cost of the entire measurement needs to be considered, and not simply the single instrument cost. More details on lidars are given in Appendix 4.

## 4. Conclusions

A number of remote sensing techniques are now available for monitoring hydrocarbons and toxic airborne pollutants. Filter and dispersive spectroradiometers with restricted versatility are sold commercially. The more versatile FTIR's and DIAL's are now becoming commercially available. Automatic, unattended field operation has been successfully demonstrated for several types of such adaptable remote sensing systems. FTIR's and DIAL's complement each other in identifying a pollutant's presence and its spatial extent; there is potential for improving their performance by a factor of ten or more in the next ten years.

Much of the promise for FTIR's lies in their reliance on computer software and hardware to perform the frequency analyses and to access the stored libraries of reference spectra. In both of these areas we can expect significant advances and cost cuts in the next ten years, judging from the past ten. Gains in optical hardware and radiation sources will also enhance FTIR performance. No "breakthrough" component development is required to enhance their present quite adequate capabilities.

DIAL performance can also be enhanced over the next ten years by about one order of magnitude with no breakthroughs. If avalanche photodiodes for the thermal infrared can be made feasible for field work, there is a potential for an additional order of magnitude or more of performance improvement. Rapid line-tuning will be easier as the development of optical modulators for the infrared progresses.

## 5. Recommendations

We recommend that EPA solicit proposals for a systems analysis of the time and costs of monitoring several problem sites or cities using existing: in situ instruments; a suite of remote sensors, and a combination of remote and in situ sensors. In this way we will obtain an objective assessment of the total time and costs to determine if remote sensing can effectively supplement environmental monitoring techniques now in use.

There are obvious improvements and modifications possible in the remote sensors described in more detail in Appendix 2. The EPA should solicit proposals for improvements in spectroradiometers and in DIALs to obtain instruments that are as perfectly matched to the Agency's requirements as technology permits. Side-by-side sensor comparison tests should continue to be run at selected industrial and toxic waste disposal sites to document the utility and capabilities of existing instruments, and of newly developed spectroradiometers and laser sensors.

When the Agency has seen demonstrated the utility of remote sensors, and it decides that remote sensors are indeed useful in accomplishing its mission, it should consider procuring a mobile spectroradiometer/DIAL system. The system would be used for continuing screening experiments, monitoring, and emergency response. As remote sensing becomes an accepted, reference technique, the use of remote sensors should be added to accepted compliance measurement methods.

## Appendix 1

### Glossary of Acronyms and Remote Sensing Terms

CLP - contract laboratory procedures
DIAL - DIfferential Absorption Lidar
DOD - U.S. Department of Defense
DOE - U.S. Department of Energy
EPA - The United States Environmental Protection Agency
EMAP - Ecological Monitoring Assessment Program
FLIR - forward-looking, infrared
FTIR - Fourier transform, infrared (spectroradiometer)
GC - gas chromatograph
IR - infrared; wavelengths from 0.75 to 15 μm in this report
laser - light amplification by stimulation of emission
lidar - light detection and ranging, usually with a laser source
MS - massspectrograph
NASA - U.S. National Aeronautics and Space Administration
NOAA - U.S. National Oceanic and Atmospheric Administration
NRC - National Research Council
ppm - parts per million by volume
ppb - parts per billion by volume
RCRA - Resource Conservation and Recovery Act
SAR - Source-Augmented Radiometer
S/N - signal-to-noise ratio
TEA - transverse-excited, atmospheric (pressure); a $CO_2$ laser
TDL - tunable diode laser
TSCA - Toxic Substance Control Act
UV - ultraviolet (wavelengths 200-400 nm or 0.2-0.4 μm here)

## Appendix 2

### Remote Sensors Capabilities List

This appendix provides in a concise form a representative list of air pollution remote sensors that exist today, their capabilities and characteristics, and where they are located. Readers of the report are encouraged to contact any of the people listed for more information. These data sheets were developed by attendees at the workshop; the list is not necessarily all-inclusive.

Each of the data sheets was provided by one of the workshop attendees. They have not necessarily been checked for accuracy, but each one reports on a different instrument with unique capabilities. Most of these instruments have already been utilized in one or more field campaigns. Information is generally available not only on the capabilities of the instrument but also on the experience of the operating crew.

The instruments are listed in order of complexity. First come the passive radiometers; next are the SAR's; and last, the laser DIAL's. Note that instrument spectral resolution is often given in "wavenumbers" or $cm^{-1}$, sometimes also termed "inverse centimeters."

| | |
|---|---|
| **Type of Instrument:** | Remote Sensing Passive FTIR spectrometer |
| **Applications:** | Site characterization, remote target component monitoring |
| **Contact person:** | Jack Demirgian |
| **Organization:** | Argonne National Laboratory |
| **Address:** | 9700 South Cass Avenue<br>Argonne, IL 60439 |
| **Telephone:** | (312) 972-6807 |
| **Fax:** | (312) 972-5287 |
| **Measuring principle:** | Infrared emission of gases |
| **Gases to be measured:** | Volatile organics |
| **Resolution/time resolution:** | 2 wavenumbers, 35 scans/sec |
| **Spectral range:** | 3500 - 2500 $cm^{-1}$ (3 - 4 μm);&<br>1250 - 800 $cm^{-1}$ (8 - 12.5 μm) |
| **Operating crew:** | One chemist |
| **Special logistics:** | Need temperature differential of 0.01°C between target and background. |
| **Potential improvements:** | Enhance qualitative identification and add quantitative capabilities. |

| | |
|---|---|
| **Type of Instrument:** | Remote Sensing Passive FTIR spectrometer (non-military version) |
| **Applications:** | Fenceline monitoring, detection of hazardous atmospheric materials |
| **Contact person:** | Robert Kroutil |
| **Organization:** | U.S. Army Chemical Research, Development and Engineering Center |
| **Address:** | Commander, US Army CRDEC<br>Attn: SMCCR-RSL/ Robert Kroutil<br>Aberdeen Proving Ground, MD 21010-5423 |
| **Telephone:** | (301) 671-3021 |
| **Measuring principle:** | Passive infrared emission of gases |
| **Gases to be measured:** | All of which absorb in the 8-12 μm region |
| **Resolution:** | 2 wave numbers |
| **Weight:** | < 30 lb |
| **Dimensions:** | 0.6 $ft^3$ |
| **Power required:** | < 10 W for interferometer @ 24 V, additional power required for portable PC |
| **Sensitivity:** | 1-30 ppm-m in the passive mode |
| **Special logistics:** | Liquid $N_2$ needed for detector |
| **Number of units:** | 2 exist (cost ~$35 K each). The optical head is commercially available from MIDAC Corp., Costa Mesa, CA. Data processing module and software available through CRDEC. |

| | |
|---|---|
| **Type of Instrument:** | Remote Sensing Passive FTIR spectrometer (military version) |
| **Applications:** | Fence line monitoring, detection of hazardous atmospheric materials |
| **Contact person:** | Robert Kroutil |
| **Organization:** | U.S. Army Chemical Research, Development and Engineering Center |
| **Address:** | Commander, US Army CRDEC<br>Attn: SMCCR-RSL/ Robert Kroutil<br>Aberdeen Proving Ground, MD 21010-5423 |
| **Telephone:** | (301) 671-3021 |
| **Measuring principle:** | Passive infrared emission of gases |
| **Gases to be measured:** | All of which absorb in the 8-12 μm region |
| **Resolution:** | 4 wavenumbers |
| **Scan time:** | 5 scans per sec |
| **Weight:** | < 50 lb |
| **Dimensions:** | 1.4 $ft^3$ |
| **Power required:** | < 80 W |
| **Sensitivity:** | military design goal < 150 $mg/m^2$ |
| **Special logistics:** | None; liquid $N_2$ for detector supplied by a Magnavox rotary cooler. |
| **Number of units:** | ~ 30 units exist |
| **Additional notes:** | This military version is called the XM-21 passive interferometer; it is designed for the automatic detection and alarm for chemical vapors; ZnSe optics; flex-pivot interferometer. |

| | |
|---|---|
| **Type of Instrument:** | Remote Sensing FTIR spectrometer |
| **Applications:** | Site characterization, remote target component monitoring |
| **Contact person:** | Bill Herget |
| **Organization:** | Nicolet Analytical Instruments |
| **Address:** | 5225 Verona Road<br>Madison, WI 53711 |
| **Telephone:** | (608) 271-3333 Fax: (608) 273-5046 |
| **Measuring principle:** | Active - longpath IR absorption<br>Passive - IR emission |
| **Range:** | Active - 0.7 km with 14.5" telescopes<br>2 km with 24" telescopes<br>Passive - depends on source emission |
| **Gases to be measured:** | Volatile organics |
| **Spectral resolution and scan time:** | 2.0 to 0.3 $cm^{-1}$ (wavenumbers),<br>~60 sec |
| **Spectral range:** | 600 to 6000 $cm^{-1}$ (1.7 - 1 μm) |
| **Detector:** | HgCdTe, $LN_2$ cooled (others available) |
| **Number of instruments:** | 5 active; 10 - 15 passive |
| **Weight:** | 150 to 200 lb (light-weight prototype being tested) |
| **Dimensions:** | 34"x26"x15" for main optical bench |
| **Power:** | 20 amps @ 110 volts |
| **Operating crew:** | Two people needed to align active system, one person for operation; one person for passive system |
| **Calibration:** | Use standard gas mixtures with internal cell or use existing reference spectra |
| **Accuracy:** | 2 - 10% |
| **Safety considerations:** | No safety problems |
| **Potential improvements:** | Total automation of data analysis procedure (preliminary software for this being tested) |

| | |
|---|---|
| **Type of Instrument:** | FTIR - Active sensing SAR |
| **Suggested applications:** | Characterization of hazardous waste site, detect target contaminants in solids such as soils and sludge; continuous emission monitoring. |
| **Contact person:** | Jack Demirgian |
| **Organization:** | Argonne National Laboratory |
| **Address:** | 9700 South Cass Avenue<br>Argonne, IL 60439 |
| **Telephone:** | (312) 972-6807 |
| **Fax:** | (312) 972-5287 |
| **Measuring principle:** | Source-augmented infrared spectro adiometer |
| **Gases to be measured:** | Volatiles and semivolatile organics |
| **Resolution/time resolution:** | 0.5 - 2 wavenumbers, 10 scans/sec @ 2 wavenumbers |
| **Spectral range:** | 4000 - 700 $cm^{-1}$, 2.5-14.3 μm |
| **Operating crew:** | One technician |
| **Special logistics:** | Liquid $N_2$ for the HgCdTe detector |
| **Potential improvements:** | Identification of non-target components |
| **Calibration method/ accuracy:** | Calibrated against a standard gas / accuracy ±2%; precision ±20%. |

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|---|---|
| **Type of Instrument:** | Automatic scanning FTIR spectrometer, with and without multiple remote sources |
| **Applications:** | Plant fenceline and operating area monitoring, emergency gas release monitoring and tracking, toxic storage and handling |
| **Contact person:** | R.L. Sandridge, R.N. Hunt |
| **Organization:** | Mobay Corporation, Research Department |
| **Address:** | New Martinsville, WV 26155 |
| **Telephone:** | (304) 455-4400 Ext. 2207 |
| **Fax:** | (304) 455-4400 Ask for FAX terminal 2438 |
| **Measuring principle:** | FTIR absorption spectra in the 8-14 μm region; computerized turret aims at remote IR sources (quantitative) or ambient background(qualitative). Emission spectra of hot plumes may also be obtained. |
| **Gases to be measured:** | All which absorb in 8-14 μm region |
| **Resolution:** | $\leq$ 1 wavenumber |
| **Time per spectrum:** | 2-4 sec |
| **Weight:** | 110 lb plus remote computer terminal |
| **Size:** | 48" high, 12"-14" diameter |
| **Power:** | 110 V, 60 Hz, 500 W (220 V, 50 Hz also) |
| **Features:** | Automatic operation, spectrum averaging, background correction, simultaneous video display of area being monitored, computer assisted calibration,scale expansion, alarm and printout functions, rugged construction. |
| **Field experience:** | Extensive field tests in industrial setting; permanent installations in U.S.A. and West Germany. |
| **Special logistics:** | Electrical power only; can run on portable field generator. |
| **Potential improvements:** | 3-5 μm operation available in near future |
| **Calibration method:** | Flow-through gas cell using standard gases; computer assisted against multiple remote sources. |

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| **Type of Instrument:** | SAR, Long-path UV absorption spectrometer, with no moving parts, 75-W xenon arc lamp retroreflector, prism, and diode array |
| **Applications:** | Plant fenceline and operating area monitoring, flux determination,collaborate with long-path IR SAR |
| **Contact person:** | Donald H. Stedman |
| **Organization:** | Dept. of Chemistry, University of Denver |
| **Address:** | University Park<br>Denver, CO 80208-0179 |
| **Telephone:** | (303) 871-3530 |
| **Measuring principle:** | Single beam gas-phase absorption |
| **Gases to be measured:** | Aromatic hydrocarbons and substituted aromatics, chlorine and aldehydes, $NO_2$, $SO_2$, and other gases with UV absorption |
| **Resolution:** | ±2 to ±20 Angstroms, selectable |
| **Weight:** | 90 lb plus personal computer |
| **Power:** | 110 V, 10 A |
| **Sensitivity:** | Noise is ~$10^3$ absorbance units (base 10) which is <1 ppb km of phenol, ~10 ppb km of benzene and toluene |
| **Field experience:** | Extensive field tests at seven hazardous waste disposal sites in NY and NJ |
| **Special logistics:** | Dry air or $N_2$ |
| **Potential improvements:** | Add long-path IR to same beam; lower power & weight, better software & library |
| **Calibration method:** | With added standard gas cells; once calibrated, the system can not lose calibration since all measurements are $I/I_o$ ratios. |
| **Number of instruments:** | One exists; ~ 2 months required to build |
| **Safety:** | Eye safe at 6 ft from xenon arc; high voltage starter for arc lamp needs careful shielding. |

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|---|---|
| **Type of Instrument:** | Laser-SAR, IR absorption radiometer, using terrain or retroreflector target |
| **Applications:** | Plant fenceline and operating area monitoring, flux determination |
| **Contact person:** | Orman Simpson |
| **Organization:** | TECAN Remote (ELS) |
| **Address:** | 3000 Northwoods Pkwy., #185<br>Atlanta, GA 30071 |
| **Telephone:** | (404) 242-0977 |
| **Measuring principle:** | Single beam gas-phase absorption, beam may be scanned through 16° x 16° |
| **Gases to be measured:** | All those that absorb at $CO_2$ laser lines |
| **Resolution:** | Width of $CO_2$ laser line |
| **Weight:** | Approximately 300 lb |
| **Power:** | 110 V, 20 A |
| **Sensitivity:** | 1 to 400 ppm-m, sensitivity is gas dependent |
| **Distance:** | 100 m to 5 km, depending on laser mode (CW or pulsed), and target used |
| **Response time:** | Less than 1 sec in most cases |
| **Field experience:** | Extensive field tests at seven hazardous waste disposal sites in NY and NJ, plus permanent installations at industrial sites |
| **Calibration method:** | With added standard gas cells |
| **Number of instruments:** | Several have been installed, mobile van available for rapid response measurements |
| **Safety:** | Eye safe at telescope aperture |

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|---|---|
| **Type of Instrument:** | Frequency agile $CO_2$ TEA lidar |
| **Suggested applications:** | Plant monitoring |
| **Contact person:** | Volker Klein |
| **Organization:** | Battelle Institute |
| **Address:** | Am Roemerhof 35<br>D-6000 Frankfurt 90<br>Federal Republic of Germany |
| **Phone:** | 49-69-7908-2859 |
| **Fax:** | 49-69-7908-80 |
| **Measuring principle:** | $CO_2$ DIAL measurement |
| **Gases to be measured:** | All which absorb in the 9-11 μm range |
| **Resolution/Time Resolution:** | $CO_2$ lines/~1 second |
| **Spectral range:** | 9R40 line to 10P40 line, 9-10 μm region |
| **Weight:** | 160 lb |
| **Dimensions:** | 40"x40"x15" |
| **Power:** | ~1.5 kW |
| **Operating Crew:** | 1 engineer |
| **Special Logistics:** | Liquid $N_2$ for the HgCdTe detector<br>(filling can be automated) |
| **Potential improvements:** | Fully automated operation |
| **Safety considerations:** | Eye-safe laser is used |

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|---|---|
| **Type of Instrument:** | Coherent-detection, dual TEA $CO_2$ lidar, MAPM (for Mobile Atmospheric Pollutant Mapping) |
| **Suggested applications:** | Emission monitoring from factories |
| **Contact person:** | Steven Alejandro |
| **Organization:** | Air Force Geophysical Laboratory |
| **Address:** | AFGL/OPA<br>Hanscom AFB, MA 01731 |
| **Phone:** | (617) 377-4774 or -3695 |
| **Fax:** | (617) 377-4498 |
| **Measuring principle:** | $CO_2$ DIAL measurement |
| **Gases to be measured:** | All which absorb in the 9.2-10.7 μm range including ethylene, methanol, ozone, organic solvent vapors, $SF_6$, vinyl chloride, hydrazines |
| **Spatial resolution:** | 50 m to 1 km depend ng on range, r, which can be 200 m < r < 3 km |
| **Spectral resolution:** | $CO_2$ lines |
| **Measurement time:** | 10 s to 1 min, depending on range; set up time for instrument is ~ 1 hr |
| **Dimensions:** | Housed in a 35x8x13½ ft semi-trailer which requires an air-ride tractor |
| **Power:** | 10 to 20kW |
| **Operating Crew:** | 1 scientist, 1 technician |
| **Special Logistics:** | Liquid $N_2$ for the HgCdTe detector, He, $N_2$, and $CO_2$ gas bottles for laser |
| **Safety considerations:** | Eye-safe laser is used |
| **Status:** | MAPM is a research instrument developed by the Jet Propulsion Laboratory for the U.S. Air Force. It was assembled using essentially off-the-shelf components to demonstrate the feasibility if such an approach. Ref.: (W.B. Grant,1989) |

| | |
|---|---|
| **Type of Instrument:** | $CO_2$ TEA lidar w/heterodyne receiver |
| **Suggested applications:** | Plume monitoring, wind measurements |
| **Contact person:** | R. Michael Hardesty |
| **Organization:** | NOAA Wave Propagation Laboratory |
| **Address:** | 325 Broadway<br>Boulder, CO 80303 |
| **Phone:** | (303) 497-6568 |
| **Fax:** | (303) 497-6750 |
| **Measuring principle:** | Doppler & $CO_2$ DIAL measurement using atmospheric aerosols as backscatter target |
| **Gases to be measured:** | All which absorb in the 9-11 μm range |
| **Resolutions:** | Range - 300m increments to 20 km range<br>horizontal, ~5km vertical<br>Wind speed - 0.5 m/s<br>Time - ~1 s |
| **Spectral range:** | 9.25 - 10.6 μm |
| **Weight:** | Housed in 20,000 lb semi-trailer |
| **Dimensions:** | 32x12x8 ft |
| **Power:** | ~5 kW |
| **Operating Crew:** | 2 experienced personnel |
| **Special Logistics:** | Liquid $N_2$ for the HgCdTe detector |
| **Number of instruments:** | One in operation |
| **Safety considerations:** | Eye-safe laser is used |

## Appendix 3

### Spectroradiometers

Introduction

Traditionally, remote sensors fall into two classes, either active or passive. An active sensor employs a transmitter to emit radiation that interacts with the target plume; then that radiation is collected by a receiver and analyzed. A passive sensor uses naturally occurring radiation, such as incident sunlight or thermal emission from the target, terrain, or the atmosphere. We see immediately that a passive sensor has the potential for being a simpler device than an active sensor since it does not need its own transmitter. In general, a passive sensor also will be lighter in weight and less expensive. Even hand-held instruments are quite feasible. Because of their long history of use, accurate calibration techniques are readily available for radiometers, such as absorption cells and blackbody sources of radiation.

However, a passive sensor is not as able to provide ranging information on the pollutant plume unless two or more are used for triangulation, and may suffer from other sensitivity problems (for example, passive thermal sensors can experience thermal washout, when the background and the target are all

at the same temperature). We will examine both active and passive spectroradiometers in this appendix. Since radiometers operate over a line-of-sight determined by the optical axis of the instrument, they are ideal for monitoring a fenceline.

## Passive Spectroradiometers

A device that measures radiation is called a radiometer. To identify a toxic pollutant we must be able to discriminate the spectrum of the radiation that it absorbs, scatters, or emits by using a spectroradiometer. There are several types of spectroradiometers that we need to consider. These are classified by the technique used to produce or identify the spectrum: filter, dispersive, gas-absorption, and interferometer instruments. Some sources of hydrocarbons and toxics such as gas flares or the warm plumes from sewage plants are by their very nature ideal targets for passive spectroradiometers. There is a wealth of experience with such devices; for example, thirty-seven different designs have been developed and tested at the U.S. Army's Edgewood Arsenal/Aberdeen Proving Ground since 1945.

## Filter Radiometers

The armed forces have been forced to face the problem of toxic plume detection even longer than civilian agencies, for chemical warfare had been a military threat since World War I. Filter spectroradiometers have been developed and field tested under the extreme environmental conditions that military operations face. Although some details of these devices are

classified, the general approach to the detection, identification, and mapping of chemical warfare plumes is well known.

A severe threat comes from the nerve agents which all contain phosphorus. The P-O-C bond in the nerve agent molecules has an absorption band within the 8-13 μm atmospheric window. The U. S. Navy has developed the AN/KAS-1 Chemical Warfare Directional Detector (CWDD) (NRC, 1984), a manually operated, filter radiometer that can monitor high concentrations of chemical nerve agents immediately after munitions have burst. These concentrations are far in excess of the amounts of toxic pollutants that the U.S. EPA will wish to detect, but the experience in developing and deploying the AN/KAS-1 (and the Forward-Looking Infrared or FLIR detectors on which it is based) is directly applicable to our problem. The three infrared filters that are sequentially inserted into the optical path of the instrument produce different contrast scenes to the observer who then determines subjectively if a nerve agent was released. Although this data processing technique is primitive, the considerable problems of deploying a cryogenic-detector, spectroradiometer in a shipboard, noisy, corrosive environment have been solved.

There are more advanced versions of such radiometers under development by the DOD. However, filter radiometers can only identify those pollutants for which an appropriate filter is available. Thus they are of limited applicability for plumes of unknown constituents. The ability to image the toxic plume is a great advantage in determining its spatial extent and to provide insight on whither it is advecting with the wind.

Infrared spectral regions are not unique in possessing absorption signatures of toxic pollutants; there are ultraviolet (UV) absorption characteristics as well in many noxious gases and vapors. The energetic UV photons allow a variety of sensors to be used, such as silicon diodes, photomultipliers and vidicons. Commercial available imaging systems can detect and display pollutant plumes using scattered UV in sunlight (Saeger et al., 1988), but such instruments may have only a limited number of pollutants that can be detected and only if the proper filters are ready to use.

## Dispersive Instruments

Dispersive instruments use either a prism or diffraction grating to disperse the frequency spectrum that irradiates the instrument into a spatial separation of frequencies. Classical spectroscopy used either photographic plates to record the spectrum, or it was scanned across a single detector for detection and recording. With our improved technology in multi-element detectors, multiplexed, parallel channels for data are feasible, thus improving the throughput of the instrument in proportion to the number of these channels. Examples of such infrared devices have been produced by the Canadian companies, Moniteq and Barringer (MONITEQ, 1986). With linear arrays of 1,000 detectors, or with spectrally coded masks used over photo-multiplier cathodes in the UV, the spectral resolution and, thus, the pollutant discrimination of most such spectroradiometers will not be competitive with interferometric instruments but may still be quite adequate for many pollutants. The simplicity of such instruments and relatively low cost of about $20K

indicates that they should not be ruled out as having a role to play for hydrocarbon and toxic pollutant remote sensing.

## Gas-Filter Correlation Instruments

These instruments use a reference cell of the gas to be sensed to provide a reference spectrum against which the spectrum from the monitored scene is to be compared. They are therefore limited to sensing only those gases for which a reference cell is available. For those specialized applications their simplicity has much to offer for their sensitivity can reach fractions of ppm levels (MONITEQ, 1986). Their incorporation into a generalized remote sensing suite of instruments cannot be recommended.

## Interferometers

The U. S. Army's XM-21 Remote Sensing Chemical Agent Alarm (RSCAAL) spectroradiometer (NRC, 1984) has been through years of development and field testing, mostly against DMMP (dimethyl methyl phosphonate), a compound that closely duplicates the spectral absorption characteristics of nerve agents.

RSCAAL operates in the 8-13 μm window using the thermal emission from the background and the toxic target. When a low-lying (thus warm) cloud of nerve agent is viewed against a clear (thus cold) sky, the contrast of the target is enhanced and detection is optimized. If there is terrain in the field-of-view, and the terrain is at the same effective radiation temperature as the cloud, then detection is not possible. However, this condition is not a

significant problem for most interferometers because the temperature difference between the cloud and the environment for a militarily-important target is less than 0.1° C. Studies of atmospheric background temperatures have indicated that a typical vapor cloud has at least a 10° C temperature difference between it and its surroundings over 99% of the measured time over all atmospheric conditions (Sutherland, 1982).

To recover the spectral information from an interferometer, the data can be processed from either the time domain or the frequency domain. The frequency domain processing generally requires a stable background emission profile that does not contain absorption features of the species to be measured. In many cases, this can be a difficult operational requirement. Modern signal processing methodology has been used to extract the signal of interest and eliminate many of the background spectral contributions (Small et al., 1988). This methodology involves the use of finite impulse response or infinite impulse response digital filters coupled with some form of automated pattern recognition technique. This signal processing methodology has been tested in several field tests in which an interferometer was mounted on a U.S. Army UH-1 helicopter and flown past a source of either DMMP or $SF_6$.

Future generations of passive interferometers will use advanced signal processing components. The digital signal processing microprocessors are a family of specialized computer chips which have gained much attention in the past several years. Their architecture has been optimized to perform instructions in a single computer clock cycle and generally concentrate on sum-of-product computations. These processors are ideal for many of the

commonly used algorithms such as impulse response filters, fast Fourier transformations, and matrix manipulations. Current performance of the small, low-cost hardware indicates that a 100-fold improvement in processor speed is available over the state-of-the-art, general microprocessors.

A number of instruments have been developed commercially (MONITEQ,1986), some for the express purpose of field detection of toxic pollutants. In the passive mode they have demonstrated the capability of ppm-m sensitivity for a number of toxic pollutants.

Source-Augmented Radiometers or SAR's

The washout problems that passive spectroradiometers may experience can be eliminated by providing such instruments with an active source. The resulting instruments can be called "source-augmented radiometers" or SAR's. Sources of radiation in the appropriate wavelength band may be located on the far side of an area that needs to be monitored, or the source and radiometers may be co-located, with only a mirror on the far side to reflect the radiation back to the receiver. Such instruments provide only a line integral average of the pollutant, but if desired (and if feasible), multiple mirrors may be located at various distances along the path to provide some range discrimination. A rigid support, such as a sturdy tripod with a pan-tilt head can serves as a mirror mount. For thermal infrared instruments, such as FTIR's, the source is usually a globar (a ceramic heater rod) equipped with a telescope collimator. Tunable laser sources can also serve for broad-band

radiometers, eliminating the need for spectral discrimination in the receiver, an instrument we may call a laser-SAR.

A source-augmented FTIR has recently been used at seven hazardous waste disposal sites in New Jersey and New York for preremedial investigations (McLaren et al., 1989). A number of compounds were identified in real-time to the ppb concentration levels. A minicomputer is required to provide the computational power to provide real-time spectra, spectrum matching, and identification. Even with present-day computers this requirement does not preclude a mobile system in a small van, and in the future much more powerful yet smaller data processors will be available. Costs for such units are in the $50K to $100K range. Future improvements and additions may double this price, but volume production will decrease it.

Industrialized versions of FTIR SAR's are already installed at several U.S.A. locations and in Europe; improved units are under development. These sensors perform automatically to detect, identify, alarm and record accidental gas releases in operating plants or along fencelines.

Augmentation can also be used in the UV, where high-pressure, xenon-arclamps provide intense sources. The other advantage to UV instruments is that the energetic photons allow the use of room-temperature, linear arrays of diode detectors. Field use of a 1024-diode silicon array in a long-path, xenon source, retroreflector instrument showed ppb sensitivity at the previously mentioned hazardous waste disposal sites (McLaren et al., 1989).

The UV electronic-transition spectra of target toxic pollutants, namely aromatic hydrocarbons, are well known and have been used for 60 years for laboratory, quantitative measurements, usually in the liquid phase; phase makes little difference for these species at moderate spectral resolution. Up to ten or more species in the same air volume may be separable. More complex mixtures may lead to some shielding of strongly absorbing species by others.

## Appendix 4

### Laser Remote Sensors

#### Introduction

Laser remote sensors or lidars for environmental monitoring have been in use since 1963, shortly after the laser was invented. There are several texts and reviews, available in most technical libraries that describe their capabilities (Gauger and Hall, 1970; Hinkley, 1976; Swain and Davis, 1978; Killinger and Mooradian, 1983; Measures, 1984; Kobayashi, 1987; Measures, 1988).

Current measurement capabilities in spectral regions that span the ultraviolet, visible, and infrared wavelengths include plume opacity, aerosol mass loading, $O_3$, $NO_2$, and $SO_2$ monitoring, even aerosol spectrometric chemical analysis by means of dielectric breakdown in a focused laser beam. In this appendix we provide more details on the status and capabilities of laser remote sensors.

DIAL

A lidar that operates with a laser at a wavelength that is absorbed by a target species and one that operates at a nearby wavelength that is not so absorbed is called a Differential Absorption Lidar or DIAL. Strictly speaking, DIALs operate using range-resolved, aerosol backscatter; terrain or mirrored return of the laser beam is also possible for improved, path-integrated sensitivity in a technique known as laser long path monitoring or more appropriately, laser SAR.

The DIAL concept was invented by Schotland (1966), and there is a wealth of experience (and of caveats) in DIAL use. To be able to map a toxic pollutant plume over distances of several kilometers with spatial resolution of a few tens of meters requires lasers of significant energy with short pulses and with mean power measured in tens of watts. Safety considerations will almost certainly demand that plume mapping DIAL's operate at "eye-safe" wavelengths where the cornea of the eye is opaque. This rules out the visible and near-IR regions.

Because many toxic pollutants have absorption bands in the wave length region 9-11 μm, a region covered by $CO_2$ lasers, and because $CO_2$ laser technology is quite advanced, it is predicted that $CO_2$ DIAL's and $CO_2$ laser long-path will be the active instruments of choice in the 1990's. Present line selection techniques, such as motor-driven micrometers or piezo-electric transducers for diffraction gratings provide for selection of about 70 lines at frequencies of a few hertz using "garden variety" $^{12}C^{16}O_2$. This frequency

of tuning is adequate for most DIAL applications. New developments of thallium arsenic selenide (TAS) acousto-optic, intracavity, tunable filters (Denes et al., 1988) promise to extend the tuning frequencies to 10 kHz as may be required for rapidly changing concentrations over short ranges, where high S/N ratios are available for each laser pulse. Rapid advances are also being made in catalytic converters for $CO_2$ lasers, so that isotopic species such as $^{13}C^{16}O_2$ and $^{12}C^{18}O_2$ will be economic, and triple the number of lines available for $CO_2$ DIAL's (Gibson et al., 1979).

CO lasers operating in the 5 μm region are also feasible. The large effort by the DOD on HF and DF lasers operating in the 3-5 μm region is resulting in commercial units that can be safely operated at these shorter wavelengths, but not yet at energies or powers suitable for DIAL. Alternatively, $CO_2$ laser frequencies may be doubled (Menyuk et al., 1976) or even tripled (Menyuk and Iseler, 1979) with efficiencies of from 5% to 10% into this spectral region. Using such a crystal in a DIAL system, Feichtneret et al. (1986) have detected ethane at a wavelength of 3.4106 μm. Optical quality $CdGeAs_2$ crystals used for this harmonic generation have been difficult to produce, however. More development support and time is required before we can predict if this DIAL approach will be a serious competitor for 9-11 μm instruments. Recently the Soviet Institute of Atmospheric Optics at Tomsk has claimed success in producing $CdGeAs_2$ crystals for frequency doubling, as well as $ZnGeP_2$ and $Te_3AsSe_3$. If the Soviet claims check out, this may point the way to greater utilization of the 3-5 μm region for DIAL or laser SAR's.

Tunable laser sources for the near and intermediate IR have also been investigated in research instruments. Menyuk and Killinger (1987) incorporated a continuously tunable Co:$MgF_2$ laser into a DIAL and demonstrated $H_2O$, HCl and $CH_4$ sensing at 40 ppm at a distance of 200 m through the atmosphere. Tuning was continuous over 1.5-2.3 μm, but the work has been halted at least temporarily. Another approach is to pump an optical parametric oscillator (OPO) with a short-wavelength laser. Eckardt et al. (1986) have demonstrated that a $AgGaSe_2$ crystal pumped by a Ho:YLF laser can produce continuously tunable energy in the 3.3-5.6 μm with pulse energies of 0.8mJ, not enough for DIAL, but pointing to technology that should be monitored during the 1990's.

There is already more than ten year's of field experience with $CO_2$ SAR's and DIAL's (Menzies and Shumate, 1976). Early work was usually done with continuous wave (CW) lasers that integrated the amount of target species between the transmitter and a mirror or terrain target, a laser SAR. Such CW lasers operate at a low plasma tube pressure, only a fraction of atmospheric. However, the significant development effort by both DOD and DOE in high-power TEA (transverse-excited, atmospheric pressure) lasers made available such units for DIAL work in the early 1980's by Killinger et al. (1983) who also demonstrated the improved signal available with heterodyne detection.

There is more averaging required with a heterodyne DIAL because the single frequency, coherent beam leads to speckle noise in the return (Hardesty, 1984), and the lidar system is also much more complex because of the requirement for diffraction-limited alignment of the transmitter and

local oscillator lasers. However, the apparent complexity of heterodyne lidars should not rule out their being reduced to reliable practice. NASA is now contracting for the LAWS (Laser Atmospheric Wind Sounder), a heterodyne lidar to fly unattended in the 1990's on the Polar Platform. The lessons to be learned in building this instrument will benefit those who wish to apply heterodyne technology for other problems, such as toxic pollutant sensing. A DIAL system that can also measure the wind in the toxic plume, an inherent ability of coherent lidars, has certain advantages in air pollution studies (Eberhard et al., 1989).

Airborne $CO_2$ DIAL's have been used to map $SF_6$ plumes (Uthe, 1986), and commercially available DIAL's or laser SAR's can be rented or custom units contracted for (Simpson, 1987). Note, however, that a DIAL must know what $CO_2$ line to tune to, and what line(s) will be at a non-contaminated reference wavelength. Present lasers can be tuned to 60 or 70 emission lines in the 9-11 μm region. If the exact constituents of the toxic plume are not known in advance, some other intelligence must be available on these constituents before a DIAL can be useful! When the constituents are known, $CO_2$ DIAL's can detect a wide variety of organic compounds and other toxic agents.

FM Laser SAR's

Frequency modulation (FM) spectroscopy using lasers is a technique where the laser is modulated at a high frequency so that the modulation frequency shows up as two sidebands on the laser line frequency. This is a laser SAR technique. If the laser is operating near the edge of an absorption line of a

target species, then the two sidebands will be differentially affected - the sideband toward the line center will be more strongly absorbed, and the one away from the line will be more weakly absorbed (Tran et al., 1984). Although the technique has been primarily used in the laboratory to date as a laser SAR, there is no reason that it cannot be extended to field, lidar use. The Electric Power Research Institute (EPRI) is now concentrating their research efforts for point measurements on this laser SAR technique (Hansen, 1988). To use this technique for a variety of target species would require that a narrow-line laser be tuned to the appropriate absorption line edge, and then frequency modulated. Demonstrated laboratory sensitivities in the parts per trillion range make this a technique to monitor closely as development progresses.

This technique may be viewed as a development over ten years old based on tunable diode lasers (TDL's) (Hinkley, 1976). Application of pressure to lead salt semiconductor lasers provides a wide tuning range. With the continual improvement in TDL's over the past few years, this technique certainly merits close tracking for application to EPA remote sensing needs.

Raman Lidar

Raman lidar detects atmospheric species by detecting the Raman-shifted backscatter (Cooney, 1970; Melfi and Whiteman, 1985). Although this molecular scattering mechanism is enhanced as the fourth-power of the frequency, the Raman cross-section remains about three orders of magnitude below Rayleigh (molecular) scattering. High power excimer lasers have recently made the

technique attractive for abundant species in the atmosphere such as water vapor (Petri et al., 1982), but it is predicted that Raman techniques will not be competitive for ppm sensing, even into the 1990's because of the extremely low backscatter coefficients and interference from aerosol fluorescence.

## Fluorescence Lidar

A fluorescence or resonance scattering lidar is one that employs the absorption and subsequent spontaneous emission of the irradiating laser photons to produce the returned signal. This technique has been used with great success in probing atmospheric constituents in the upper atmosphere (Megie, 1988). However, this technique does not work well in the lower atmosphere because the higher pressure almost always leads to quenching collisions with the excited molecule before it has a chance to emit its characteristic radiation. The technique may have some limited application in the detection of aerosols, dusts, and films, but there is little chance that it has application for airborne, hydrocarbon or toxic pollutant plumes, except when fluorescent aerosols are intentionally injected into the plume as a sensible tracer.

## Appendix 5

### Examples of Remote Sensor Successes

During early autumn of 1988, measurements of airborne toxic pollutants and hydrocarbons were conducted at seven potential Superfund sites in New York and New Jersey (Minnich et al., 1989; McLaren et al., 1989). The FTIR SAR used during these field measurements detected eight different compounds, all in the low ppm-m range, listed in Appendix 7. Path lengths up to 400 m to the folding mirror were used. Set up time was less than one hour after arriving at each site. A standard Nicolet Model 730 FTIR system was used, supplemented by 37 cm aperture Cassegrain telescopes for both the radiometer and the globar source. Signal processing electronics included an 18-bit analog/digital converter and a Nicolet 620 data station that is built around a minicomputer with 50 m byte hard disk.

The success obtained in identifying pollutants during these field tests indicates that FTIR remote sensing techniques are at a stage of maturity that enable significant results to be quickly obtained for concentration levels of importance in monitoring toxic waste sites. In addition, visible and near-IR lidars have long been used for studying pollutant transport and diffusion in plumes and air masses (e.g., Eberhard and McNice, 1986; Wakimoto and McElroy, 1986; McElroy and Smith, 1986; McElroy, 1987) or fluorescent tracers in such

plumes (Uthe, et al., 1985). This substantiates the statement made earlier, that remote sensing is not an "ivory tower" concept, but one that is now ready to help solve EPA hydrocarbon and toxic pollutant sensing problems.

The NOAA Wave Propagation Laboratory's pulsed Doppler lidar uses a coherent $CO_2$ laser at 10.6 μm wavelength. The lidar measures the back-scattered radiance to determine turbidity from large aerosols and also determines the wind field. This is accomplished by measuring the Doppler frequency shift caused by the scattering aerosols' motion as they advect with the wind. A range-resolved component of the wind parallel to the laser beam can be displayed in real time at slant ranges of 20 km or more in the lower atmosphere. A number of successful experiments have been accomplished since the lidar was placed in operation in 1981 (Hall et al., 1987). IR DIAL measurements are accomplished by time sequencing the laser between absorbing and window lines.

This lidar participated during December 1987 as part of the Denver Brown Cloud Study, documenting the meteorology of aerosol and CO polluting events during wintertime in a high-elevation metropolitan region (Eberhard et al., 1989). The lidar mapped the aerosol cloud out to distances of typically 20 km in north-east Denver. Simultaneous wind data from the lidar revealed much about the associated mesoscale meteorology. The lidar confirmed the existence of a weak drainage flow toward the northeast, followed by a return flow driven by typical pressure gradients that carry polluted air back to Denver. It also showed how stagnant, polluted air could cover part of the metropolitan area

while clean air was present in other zones where strong mountain winds extended to the surface.

## Appendix 6

### Future Improvements Possible in Remote Sensor Performance

In this appendix we examine the performance equations of the promising remote sensors discussed in Appendices 3 and 4 to understand where improvements in performance may be expected in such instruments over the next five to ten years.

#### Spectroradiometers

There are fundamental, physics-imposed limitations to radiometer performance. These can be best studied by examining the S/N (signal-to-noise) equations that apply to radiometers. First, an equation that applies to any type of radiometer is presented. The nomenclature of Silva (1978) is used to show that the noise equivalent power (NEP) of a photon-detector radiometer is,

$$NEP = \frac{(A \cdot \delta F)^{1/2}}{D^*}$$

where A is the area of the detector, $\delta F$ is the electronic bandwidth of the radiometer amplifier, and $D^*$ is the detectivity of the detector. The value of $D^*$ is, of course, a function of wavelength, but we will not list this subscript to avoid clutter in the equations. Detector area, A, is related to

the field of view (FOV ≡ $\theta$) of the radiometer, and the effective optics focal length, f by,

$$\theta \quad \sqrt{A}/f$$

since the detector is the limiting field stop, and the FOV is usually small. The effective focal length is used because most radiometers do not form an image of the source onto the detector but rather use field lenses or condensing optics to increase the "speed", $\Sigma$, or f/ratio of the optics. $\Sigma \equiv D/f$, where D is the entrance aperture diameter.

The input-signal power, $\Phi$, to the audiometer detector over the spectral increment employed is,

$$\Phi = \tau_a L \pi D^2 \theta^2 \varepsilon / 4$$

where $\tau_a$ is the atmospheric transmittance from the source to the radiometer, L is the radiance of the source, and $\varepsilon$ is the optical efficiency of the radiometer. In order to maximize

$$S/N = \Phi/NEP = \frac{\pi_a L D \Sigma \theta \varepsilon D^*}{4(\delta F)^{1/2}}$$

the numerator terms must be made as large as possible and the denominator as small as possible. Only the numerator variables can be improved, for the electronic bandwidth is determined by the "scan" time, which is in turn dictated by inherent atmospheric variability in the pollutant volume or by the

time available to measure the plume from different aspects, and these times will probably not change over the next ten years.

Taking the numerator terms in order, first, the wavelength increment in the atmosphere that has maximum transmittance must be used, but since the 8-13 μm window is already used in many devices, and the transmittance is close to 1.0 over path lengths of a few kilometers, there is not much optimizing left to do with $\tau_a$. With passive radiometers, there is not much that can be done with the source radiance, L, since this is most often the Planckian thermal scene radiance. With source-augmented radiometers, however, there are improvements that can be made. The globar sources commonly used for FTIR's operate at a maximum temperature of about 1400K. As pointed out by Smith et al. (1957) specially constructed tungsten, v-grooved filament lamps can operate at more than twice this temperature. Experimental tests show an 8-13 μm radiance twice that of globar. With the improvements in IR window materials in the past 20 years, only a modest amount of development effort should be needed to improve sources for augmented radiometers. Increasing L by a factor of 2 provides 3 dB more signal.

Some improvement in D* can be expected, but many detectors are already very close to the quantum noise limits. Improvements in cryogenic enclosures and radiation shields can offer some improvement for thermal-IR detectors, and these may improve D* by a factor of 2, or 3 dB in signal strength.

Note that if a radiometer could be devised which employed multiple detectors for examining the pollutant volume, the S/N improves as the square-root

of the number of detectors, because the signal in each of the detectors is correlated but the noise is not. One technology that has seen dramatic improvement in the past few years, and that promises to continue improving in the future is in the ability to produce multi-element, solid state detectors in linear or areal arrays. It seems reasonable to forecast that in five to ten years arrays of ten to thirty times greater complexity than present designs will be available. What is not obvious is how to advantageously employ multiple element detectors in FTIR's, although they could be used to average-out speckle noise in coherent DIAL's; multiple detectors have already proven their advantage in dispersive instruments.

Another improvement may come from the optics aperture. Light-weight optics are another area where significant recent improvements have been shown, with further advances most probable. In field instruments it is often the weight of the device that limits its utility, so larger optics diameters need not impact on an instrument's mobility. An increa of D by a factor of 2 is an easy way to achieve another 3 dB of signal. So if we add together all of these improvements, we find that 9 dB (or a factor of nearly 10) can be expected over the next few years in radiometer sensitivity enhancement.

Since FTIR performance is strongly determined by digital computing speed and by software sophistication, it is predicted that a future FTIR will be improved overall in three categories: (1) In the number of pollutants that it can store in memory for real-time identification, (2) In the speed with which these identifications can be made, and (3) In improved sensitivity into the fraction of ppb range - the 9 dB, or factor of nearly ten, enhancement

predicted above. There are no critical component weaknesses to exploit in order to achieve greater improvements. Costs of mobile FTIR's with their real-time computers will be in the range of $50K to $200K, 1988 dollars. UV dispersive instruments should be somewhat less expensive.

Laser Remote Sensors

The S/N equation for a lidar is not too different than that for a radiometer since the lidar receiver is really just a radiometer adapted for the high frequency response required to achieve adequate range resolution. Since the laser radiation backscattered from atmospheric or topographic targets decreases as the inverse-square of the range, R, to the scatterer, the energy, E, returned to the detector is,

$$E = E_L \varepsilon \tau_a R^{-2} (\pi D^2/4) \beta (ct/2)$$

where $E_L$ is the energy in the laser pulse of duration t, $\beta$ is the backscatter coefficient of the target, c is the velocity of light, and the other symbols have the same meaning as on pgs. 48-49. This returned energy is converted to a signal current, $i_s$, according to the expression,

$$S \equiv i_s = \Phi \Gamma$$

where the signal power is simply $\Phi = E/t$ and $\Gamma$ is the responsivity of the detector and amplifier (usually given in amperes per watt).

The predominant noise term appropriate for the lidar equation will vary according to the spectral region and thus the type of detector that will be used (Hall, 1974). In general, the noise can be attributed to a sum of these noise currents,

$$N \equiv i_n = [2e\delta F(i_s + i_b + i_d)]^{1/2}$$

where e is the electronic charge, and the subscripts b and d stand for background and dark respectively.

When looking for those improvements in lidar (DIAL) system performance that may be expected over the next ten years, it is expected that improved light weight optics will make an increase in D possible without impacting the system mobility. An increase in optics area by a factor of 2 for a 3 dB gain in signal will be feasible. The energy available from line-tunable or continuously tunable sources will also increase as laser efficiencies and materials are improved, both for gaseous and solid state units. An improvement in energy by a factor of 3, or 5 dB is frugal.

The potential for the greatest improvement breakthrough exists with infrared detectors. Present detectors, such as the ubiquitous HgCdTe operated at 77°K have an extremely low responsivity, and therefore require high-gain preamplifiers before the signals can be operated upon. But to achieve the frequency response required for a pulsed DIAL, the fundamental Johnson noise in the preamp swamps the meager detector signal. This is the principal reason why heterodyne systems have been developed, to amplify

optically the signal to a level where the preamp noise is negligible. Avalanche photodiodes are just becoming available in the near infrared (Brown and Ridley, 1986), and liquid helium-cooled devices have been demonstrated for the thermal infrared (Stapelbroek, 1987). If a practical, field-deployable, avalanche detector can be developed for $CO_2$ DIALs, the sensitivity of a heterodyne DIAL may be approached without the speckle limitations or the complications of interferometer alignment. Sensitivity could then be increased by a factor of 10 to 100 (or equivalently, 10 to 20 dB).

Overall lidar or DIAL sensitivity can be expected to improve by a factor of six (or 8 dB) in the next ten years without detector improvements. If avalanche detectors become available, the total improvement could be factors of 60 to 160 (or 18 to 28 dB). These 1990's DIALs will also be much more versatile, reliable, and sophisticated compared to today's units.

Laser remote sensor overall performance can thus be improved in three categories also: (1) In the number of lines that can be tuned to quickly, from the present 70 or so to perhaps 200 for $CO_2$ instruments (by using isotopes of $CO_2$; prototypes of such lasers have been built) and over wider increments in the UV, visible, and near IR using new solid state lasers, (2) In the speed with which this tuning can be accomplished, and (3) In sensitivity into the fraction of ppm range for sensing ranges of several kilometers and into the ppb range for shorter ($\sim$ 10 m to 100 m)ranges. $CO_2$ laser technology is more advanced than competing sources for DIAL, and will likely remain so into the 1990's. Avalanche detectors present a critical component development opportunity for thermal IR DIAL's, and much work remains on improving tunable diode

and tunable solid state lasers. Costs for mobile $CO_2$ DIALs will be in the $150K to $500K range in 1989 dollars.

## Appendix 7

**Remote Sensing Detection Levels for Hydrocarbons and Toxics**

The table that follows lists examples of compounds that have been detected using existing sensors under field conditions.

| Pollutant | Absorption Spectrum Band, μm | Spectro-radiometer Detection Limit | Laser(DIAL) Sensor Detection Limit | Reference |
|---|---|---|---|---|
| Phosgene | 11.8 | ~1 ppm.m | | Mobay Corporation (see p.20) |
| CFC-11 | | ~1 ppm.m | | " |
| CFC-12 | | ~1 ppm.m | | " |
| $NH_3$ | 10.4, 10.7 | ~1 ppm.m | | " |
| Ethylene oxide | 10.7-11.9 | ~30 ppm.m | | "<br>" |
| Propylene oxide | 11.4-12.2 | ~30 ppm.m | | "<br>" |
| o-xylene | 7.1-14.3 | ~33 ppm.m | | Minnich et al. (1989) |
| Toluene | " | ~10 ppm.m | | " |
| Chloroform | " | < 4 ppm.m | | " |
| Methanol | " | ~1.4 ppm.m | | " |
| Acetone | " | ~23 ppm.m | | " |
| p-xylene | " | <30 ppm.m | | " |
| 1,1,1-tri-chloroethane | " | ~3 ppm.m | | " |
| 1,3,5-tri-methylbenzene | "<br>" | <3 ppm.m | | " |
| Ethylene | 10P(14),(12) | | 0.3 ppm.m | Grant (1989) |
| Trichloro-ethylene | 10P(20),(10) | | 0.9 ppm.m | " |
| Chloro-benzene | 9R(26),9P(12) | | 5.3 ppm.m | " |

## Appendix 8

Attendees at the EPA Workshop on Remote Sensing of Hydrocarbons and Toxic Pollutants, Las Vegas, Nevada, 6-7 April 1989.

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| | |
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| | |
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| | |
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